

Phase-field modelling of oxide growth on chromium-rich alloys

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Context

ANR RaccOon – RelAtions miCrostructure méCanique OxydatiON



Objectives: **Describing, characterizing and modeling** the multi-physics couplings during high temperature oxidation in **model systems (**Alloys Fe-25Cr and Fe-25Cr-1Si).

WP1 (SIMaP/UTC): Characterizing mechanisms under mechanical loadings → growth kinetics and morphologies of oxides layers.

WP2 (UTC/SIMaP): Linking the oxidation-induced microstructure to the local mechanical properties.

WP3 (ONERA/SIMaP): Modeling (multi-phase field, multi-components, mechanics) → kinetics and morphologies

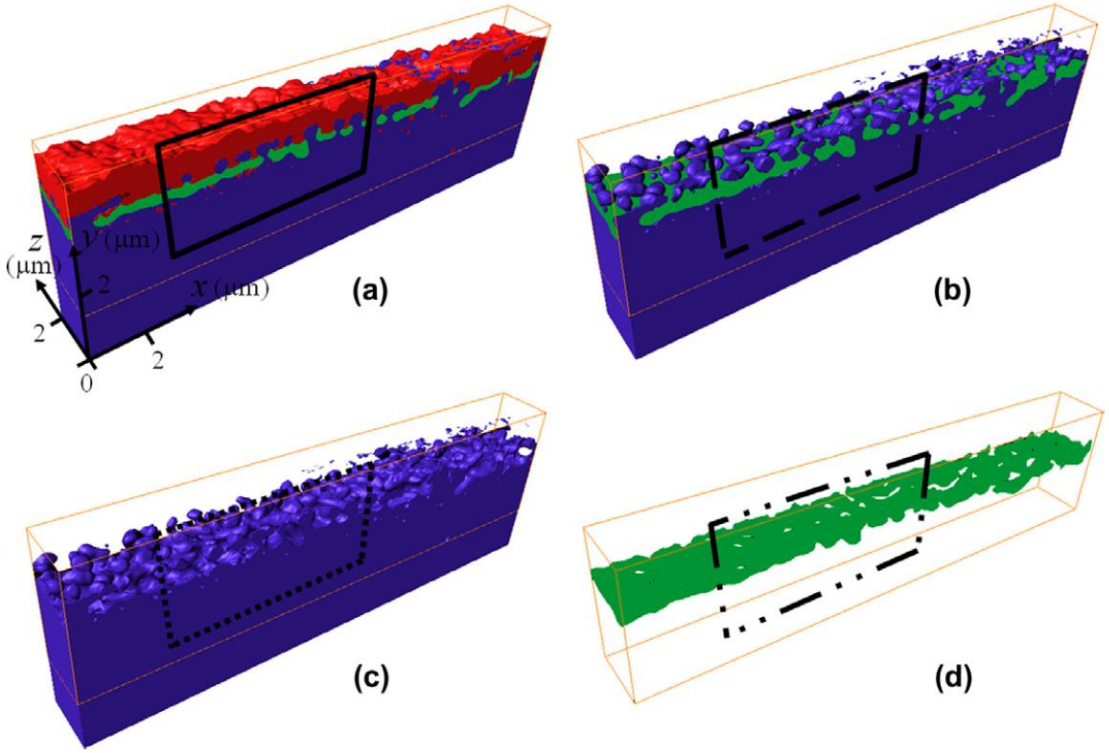
SIMaP

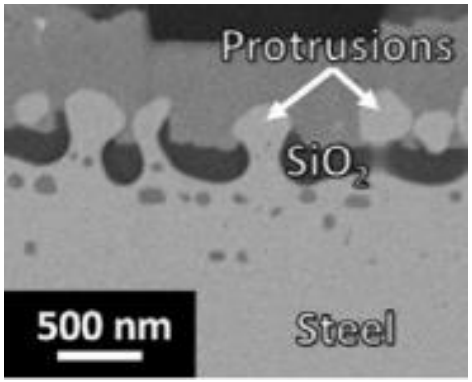
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Context

- For **Fe-16Cr-1Si**, specific interfacial morphologies can be observed resulting from the coupling between oxidation and mechanics; explanation?



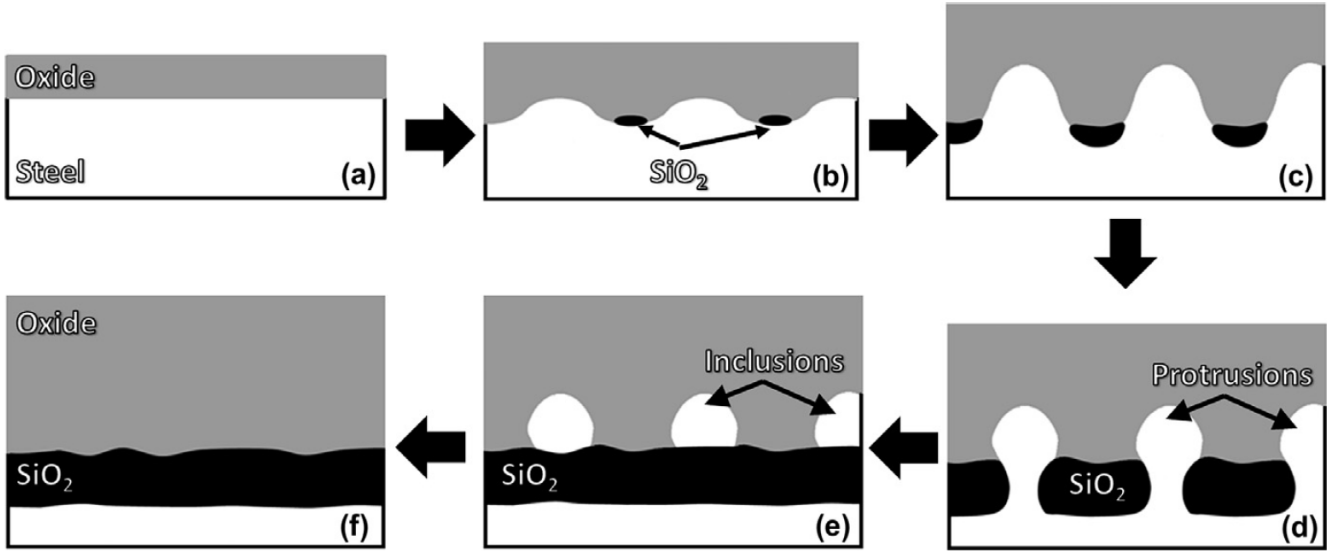


SEM cross section of the oxide layer on Fe-18Cr-Si steel at high temperature

Issartel et al. (2012). Corrosion Science, 59, 148-156

Context

- Proposed mechanism based on post-mortem observations and static elastic calculations allowing to identify lower tensile zones where the oxygen is expecting to go:



- Does wrinkling result from a mechanical instability allowed by a creep-induced softening of the metal? Does the oxygen preferentially go in the grooves of wrinkles? What are the main driving forces leading to protrusions?

- We need a model able to couple the multiple diffusion-induced phase evolution with mechanical effects (that ultimately includes finite strains and creep!)

Issartel et al. (2012). Corrosion Science, 59, 148-156

Outline

1. **Multi-phase fields and multi-component model**
    1. Fields and energies
    2. Kinetics
    3. Some tests

2. **Growth kinetics of on oxide layer in 1D**
    1. Binary model case (2 phases) *without elasticity*
    2. Ternary case (Cr_2O_3 / Alloy) *without elasticity*
    3. Quaternary case (Cr_2O_3 / SiO_2 / Alloy) *without elasticity*
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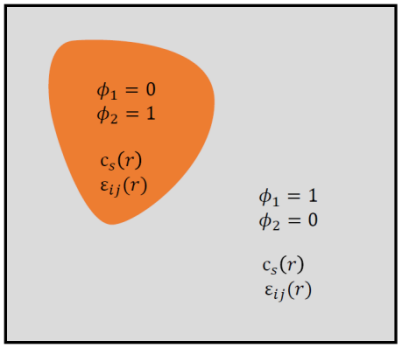
Conclusion

Multi-phase fields and multi-component model

- **Fields:**

  - Phases $\phi_p(\boldsymbol{r})$ with $p = 1, \dots, N_p$
  - Atomic concentrations $c_s(\boldsymbol{r})$ with $s = 1, \dots, N_s$
  - Strains $\varepsilon_{ij}(\boldsymbol{r})$

$$\sum_p \phi_p(\boldsymbol{r}) = 1$$



- **Free energy:** $F = \int_V \{f_{elas}(\{\phi_p\},\{\varepsilon_{ij}\}) + f_{int}(\{\phi_p\}) + f_{chem}(\{\phi_p\},\{c_s\})\}\, dV$

$$f_{elas} = \frac{1}{2}\left[\Lambda^{ref}_{ijkl} + \sum_p h(\phi_p)\left(\Lambda^{(p)}_{ijkl} - \Lambda^{ref}_{ijkl}\right)\right]\left[\varepsilon_{ij} - \sum_p h(\phi_p)\varepsilon^{0(p)}_{ij}\right]\left[\varepsilon_{kl} - \sum_p h(\phi_p)\varepsilon^{0(p)}_{kl}\right]$$

$$f_{int} = \sum_{p<q}\left(A_{pq}V(\phi_p)V(\phi_q) - \lambda_{pq}\nabla\phi_p \cdot \nabla\phi_q\right)$$

$$f_{chem} = \sum_p h(\phi_p) f^{(p)}(c_s)$$

At lowest order, the chemical free energy of a phase can be approximated by:

$$f^{(p)}(c_s) = \hat{f}^{(p)} + \sum_s \frac{1}{2} k_s^{(p)} (c_s^{(p)} - \hat{c}_s^{(p)})^2$$

Intermediate fields $c_s^{(p)}$ are calculated by using the KKS constraints*:

$$c_s = \sum_p h(\phi_p)\, c_s^{(p)} \qquad \tilde{\mu}_s = \tilde{\mu}_s^{(1)} = \tilde{\mu}_s^{(2)} = \cdots = \tilde{\mu}_s^{(N_p)}$$

*Kim et al. (1999). Physical review E, 60(6), 7186

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Multi-phase fields and multi-component model

- **About** $f_{int} = \sum_{p<q} \left(A_{pq} V(\phi_p) V(\phi_q) - \lambda_{pq} \nabla\phi_p \cdot \nabla\phi_q \right)$

In a two-phase system, the usual choice $V(\phi_p) = 4\,\phi_p^2$ with $\phi_2 = 1 - \phi_1$ leads to the well-known profile:

$$\phi_1 = \frac{1}{2}\left(\tanh\left(\frac{2x}{\xi}\right) + 1\right)$$

Interface width

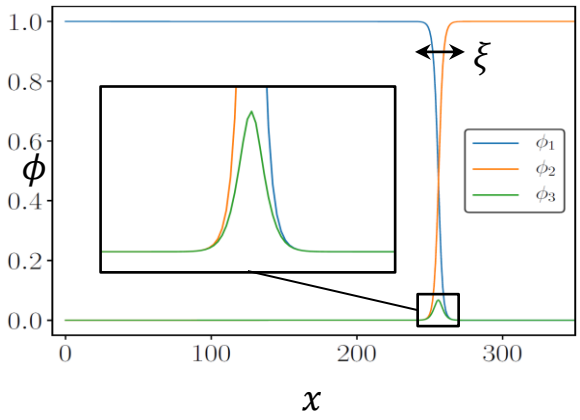
$$\xi = \sqrt{\frac{\lambda_{12}}{A_{12}}}$$

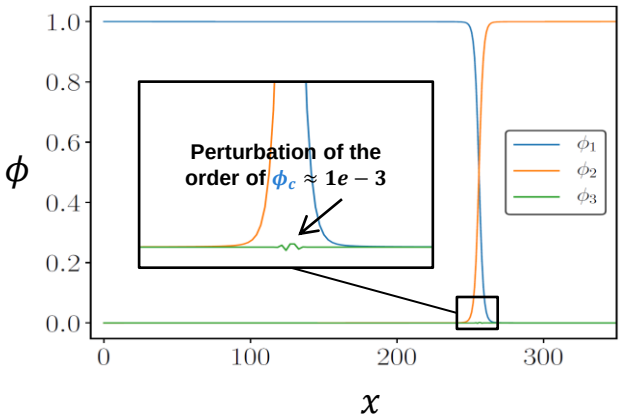
Interface energy

$$\gamma_{12} = \frac{4}{3}\sqrt{A_{12}\,\lambda_{12}}$$

These relationships are wrong when $N_p > 2$ (“ghost phases”)

Our solution: $V(\phi_p) = 4\,\phi_p^2$ ⇒ $V(\phi_p) = 4\,\phi_p\, f_{sat}(\phi_p, \boldsymbol{\phi_c})(1-\phi_p) f_{sat}(1-\phi_p, \boldsymbol{\phi_c})$







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Multi-phase fields and multi-component model

- **Kinetics:**

Mechanical fields evolve quasi-statically:

$$\nabla \cdot \boldsymbol{\sigma} = 0 \qquad \langle \boldsymbol{\sigma} \rangle = \boldsymbol{\sigma}^{App}$$

Phase fields are controlled by a relaxation equation (Allen-Cahn):

$$\frac{\partial \phi_p}{\partial t} = -\sum_q L_{pq}\left(\frac{\delta F}{\delta \phi_p} - \frac{\delta F}{\delta \phi_q}\right) \quad \text{with} \quad L_{pq} = L_{qp} \quad \text{et} \quad \forall q, \sum_p L_{pq} = 0 \qquad \sum_p \phi_p(\boldsymbol{r}) = 1$$

L_{pq}: mobility of fields

Atomic concentrations are controlled by a conservation equation:

$$\frac{\partial c_s}{\partial t} = -\nabla \cdot \boldsymbol{J}_s \quad \text{with} \quad \boldsymbol{J}_s = -M_s(\phi_p)\nabla \frac{\delta F}{\delta c_s} \quad \text{where} \quad M_s(\phi_p) = \sum_p h(\phi_p)\, M_s^{(p)}$$

$$M_s^{(p)} = \frac{D_s^{(p)}}{k_s^{(p)}}$$

$D_s^{(p)}$: diffusivity

$M_s^{(p)}$: mobility of the species "s" in phase (p)

$k_s^{(p)}$: "curvature of the chemical free energy"

Remark 1: When $L_{pq} = L$, plane interface mobility μ is related to the phase mobility L with the relationship $\boxed{\mu = \frac{3N_p}{4}\,\xi\, L}$

Remark 2: When the interface movement is only controlled by the species diffusion, L is taken large enough, so it no longer affects the results.

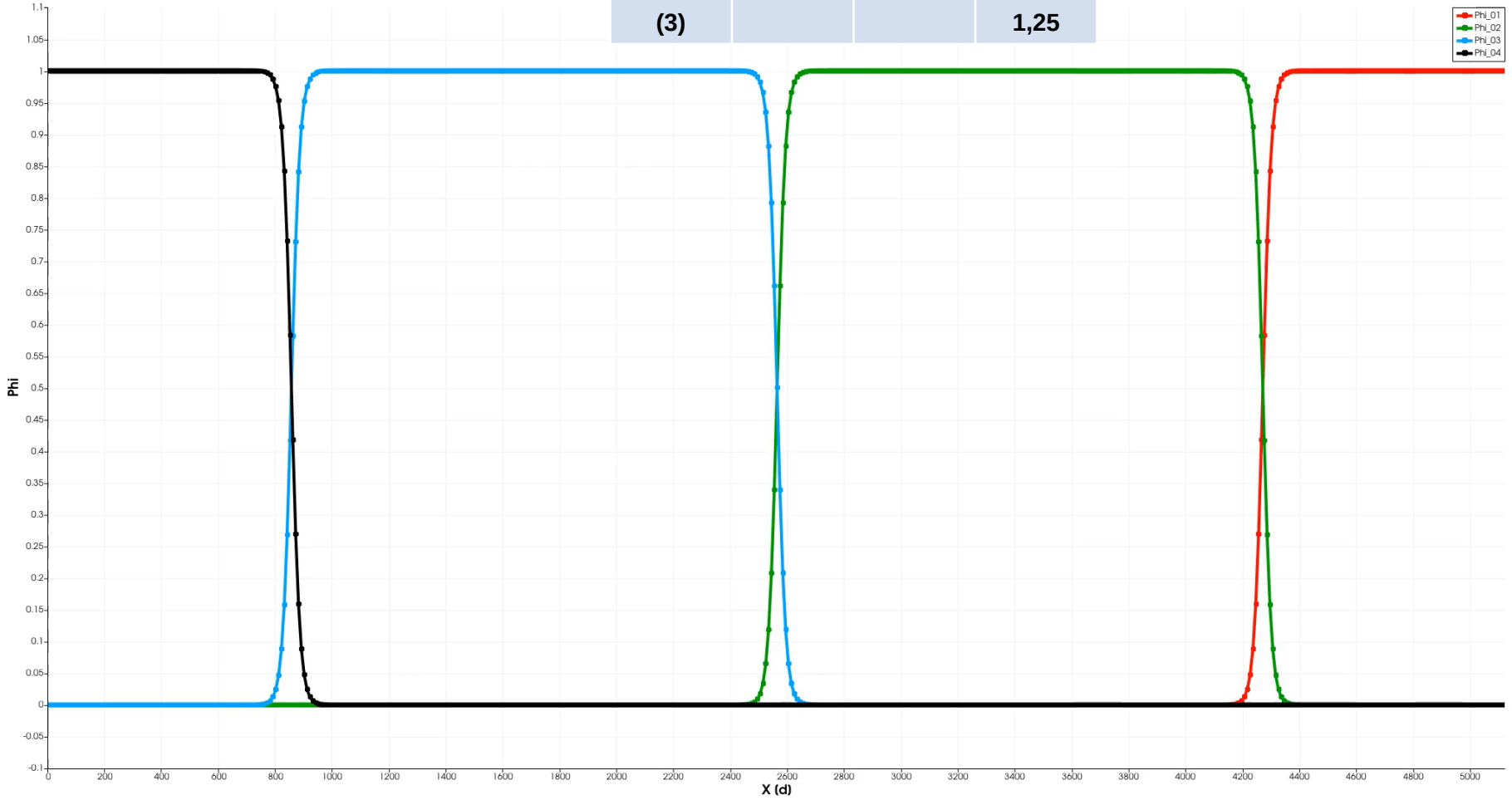
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Multi-phase fields and multi-component model

- **Some tests**

γ [J/m²]	(2)	(3)	(4)
(1)	1	2	3
(2)		1,5	2,5
(3)			1,25

Kinetics ok



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Multi-phase fields and multi-component model

- **Some tests**

N°	γ_{12}/γ_{13}	γ_{23}/γ_{13}
1	0,5	0,5
2	1	0,5
3	1,5	0,5
4	0,5	1
5	1	1
6	1,5	1
7	0,5	1,5
8	1	1,5
9	1,5	1,5

- Case (2,5,8) → $\gamma_{12} = \gamma_{13}$

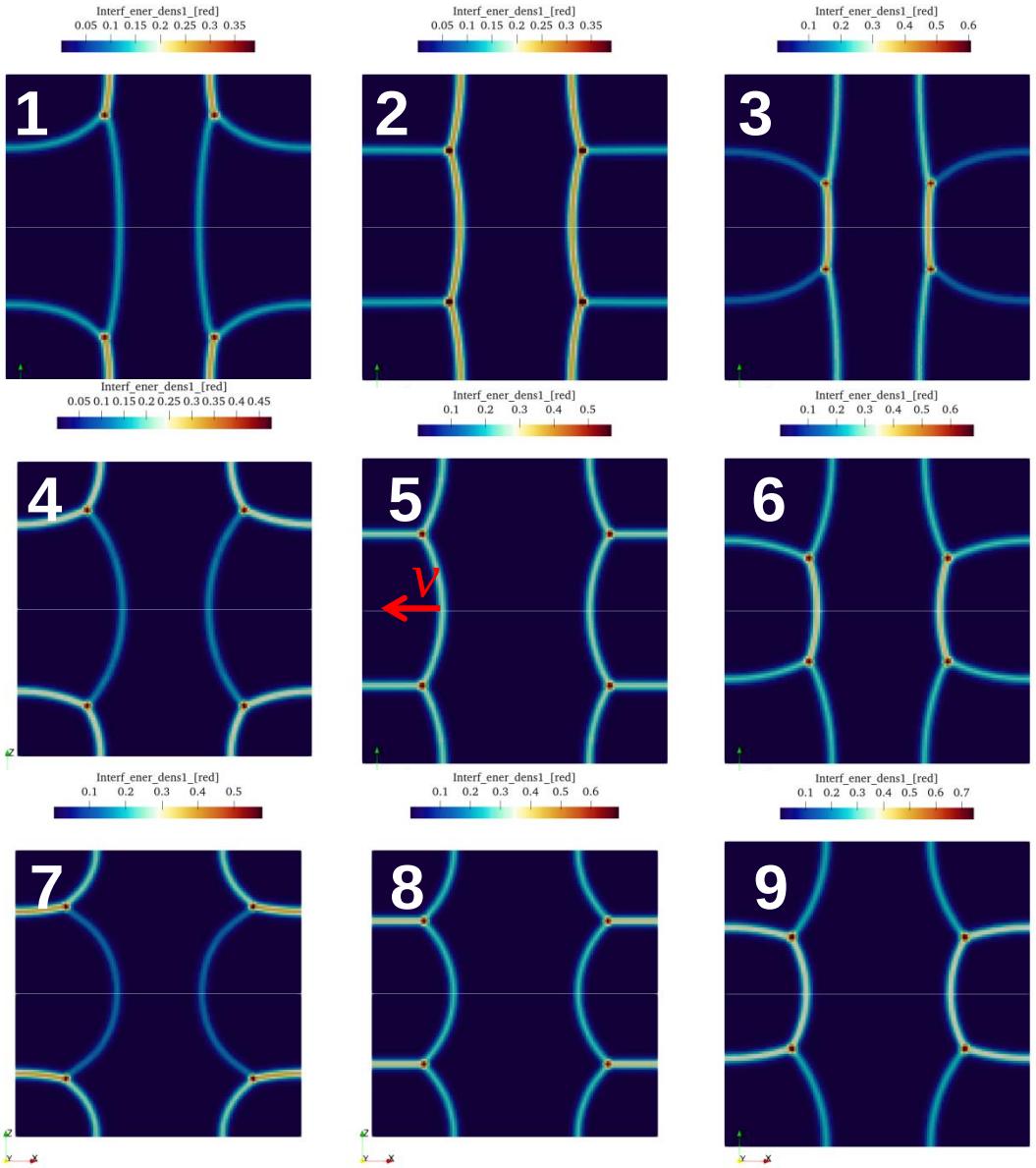
Young-Laplace's law:

$$\theta_{23} = \cos^{-1}\left(\frac{\gamma_{23}}{2\,\gamma_{12}}\right)$$

Velocity of the midpoint:

$$v = \frac{M\,\gamma_{12}}{y_0}\left(\frac{\pi}{2} - \theta_{23}\right)$$

Morphologies and kinetics ok



Outline

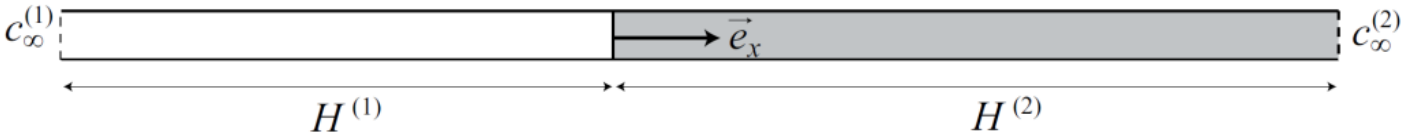
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Conclusion

Growth kinetics of on oxide layer in 1D

- **Binary model case (2 phases) without elasticity**



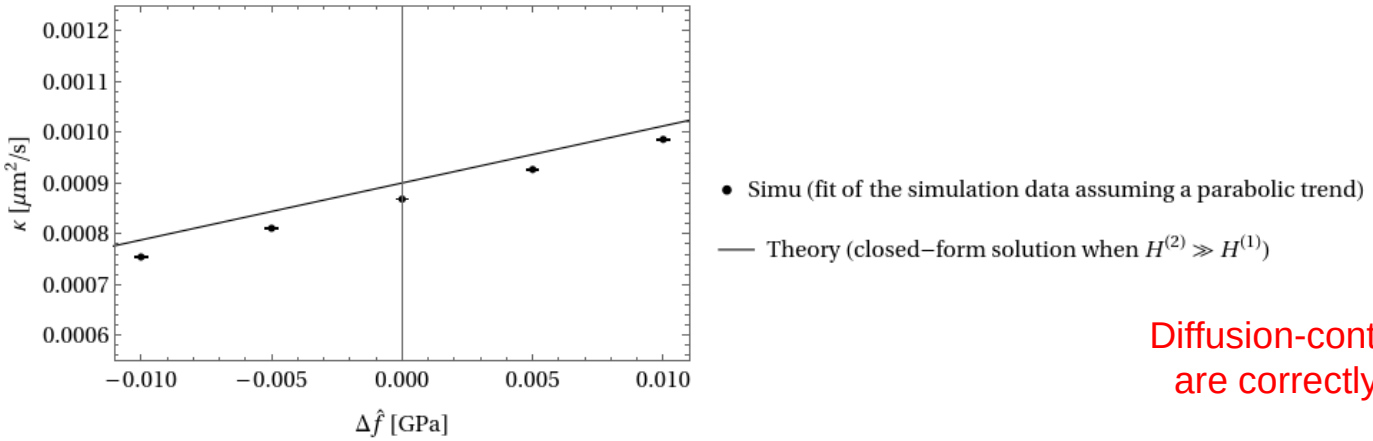
Under the "local equilibrium assumption", when $H^{(2)} \gg H^{(1)}$, the interface velocity is such that:

$$\left(H^{(1)}\right)^2 - H_0^2 = \kappa_{chem}\, t \qquad \text{with}$$

$$\kappa_{chem} = 2\, D^{(1)} \left(\frac{\hat{f}^{(2)} - \hat{f}^{(1)}}{K^{(1)} \left(\hat{c}^{(2)} - \hat{c}^{(1)}\right)^2} - \frac{c_\infty^{(1)} - \hat{c}^{(1)}}{\hat{c}^{(2)} - \hat{c}^{(1)}} \right)$$

Growth rate

Comparison simulation vs. theory:

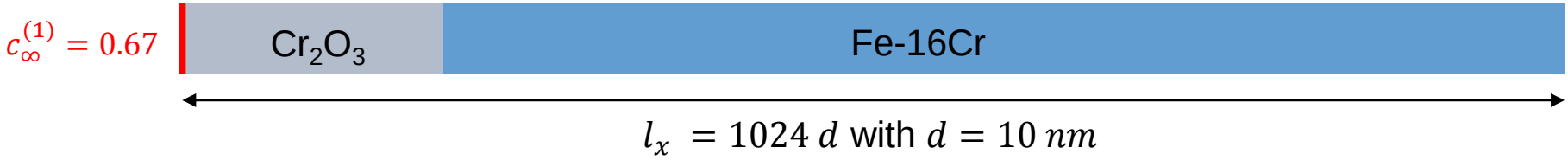


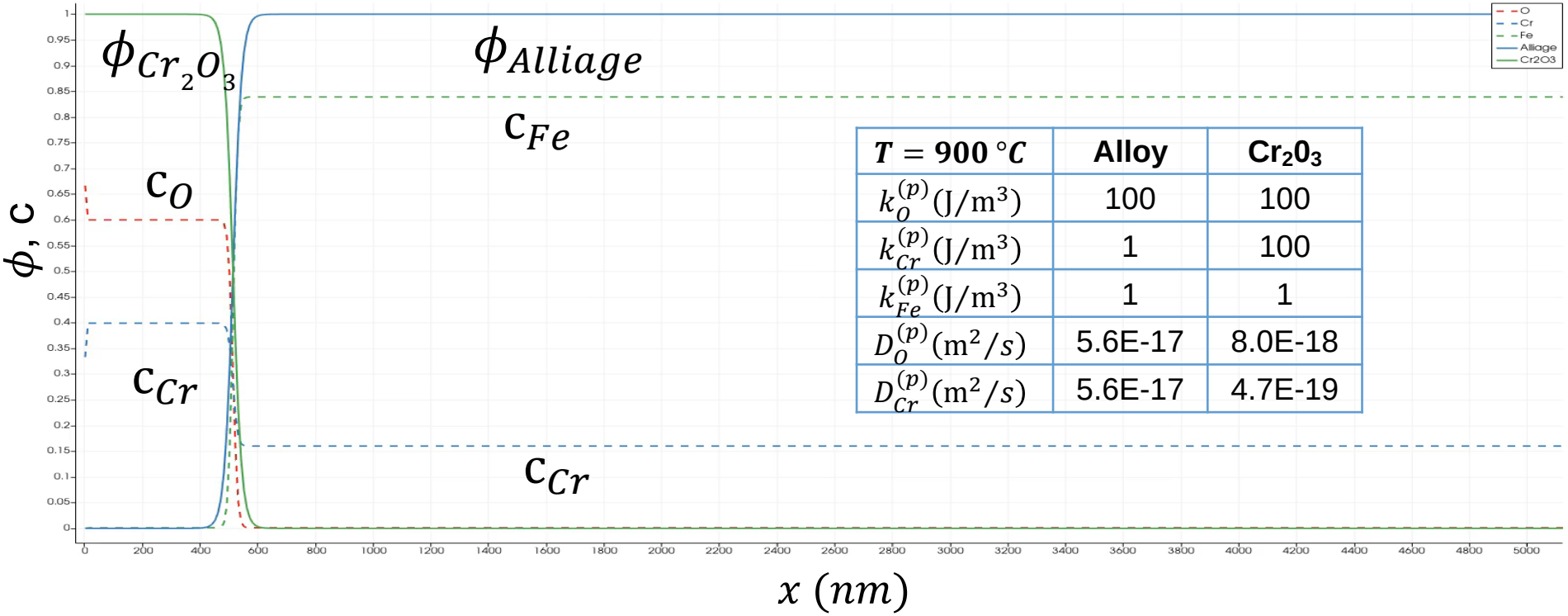
Diffusion-controlled kinetics are correctly reproduced

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Growth kinetics of on oxide layer in 1D

- **Ternary case (Cr_2O_3 / Alloy) without elasticity**





$T = 900\,°C$	Alloy	Cr_2O_3
$k_O^{(p)}(\mathrm{J/m^3})$	100	100
$k_{Cr}^{(p)}(\mathrm{J/m^3})$	1	100
$k_{Fe}^{(p)}(\mathrm{J/m^3})$	1	1
$D_O^{(p)}(\mathrm{m^2}/s)$	5.6E-17	8.0E-18
$D_{Cr}^{(p)}(\mathrm{m^2}/s)$	5.6E-17	4.7E-19

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Growth kinetics of on oxide layer in 1D

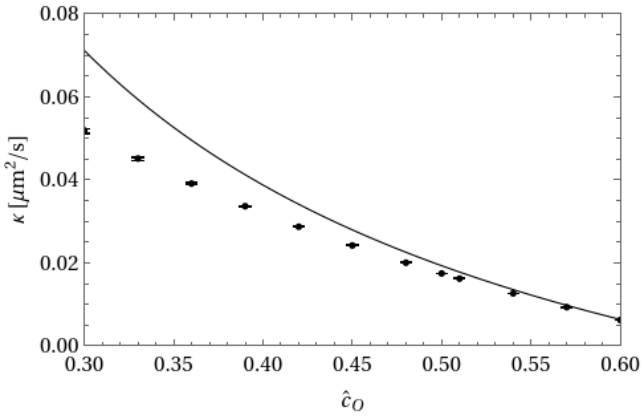
- **Ternary case (Cr_2O_3 / Alloy) without elasticity**



The theoretical growth rate can be estimated by considering that the chrome is the component that limits the diffusion (De Rancourt's thesis – 2016):

$$\kappa_{chem} = 4\, D_{Cr}^{(2)} F^{-1}\left(\Omega_{Cr}^{(2)}\right)^2 \qquad F(x) = x\sqrt{\pi}\exp(x^2)\,\mathrm{erfc}(x) \qquad \Omega_{Cr}^{(2)} = F\left(\sqrt{\frac{1}{2}\frac{D_O^{(1)}}{D_{Cr}^{(2)}}\Omega_O^{(1)}}\right) \qquad \Omega_O^{(1)} = -\frac{c_{\infty O}^{(1)} - \hat{c}_O^{(1)}}{\hat{c}_O^{(2)} - \hat{c}_O^{(1)}}$$

Comparison simulation vs. theory:



- Simu (fit of the simulation data assuming a parabolic trend)

— Theory (closed–form solution when $H^{(2)} \gg H^{(1)}$)

The growth rates are very sensitive to the input parameters…

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Growth kinetics of on oxide layer in 1D

- **Quaternary case (Cr_2O_3 / SiO_2 / Alloy) without elasticity**



Thermo-kinetics data and initial condition: as before

What about the diffusivity (T = 900 °C)?

	Alloy (1)	SiO_2 (2)	Cr_2O_3 (3)
$D_O^{(p)}(\mathrm{m}^2/s)$	5,60E-17	**4,70E-19**	8,00E-18
$D_{Cr}^{(p)}(\mathrm{m}^2/s)$	5,60E-17	**?**	4,70E-19
$D_{Fe}^{(p)}(\mathrm{m}^2/s)$	**1,87E-14**	**1E-24**	**?**

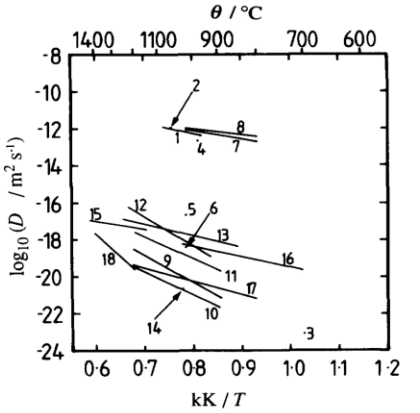


Fig. A1. Oxygen transport in amorphous silicon dioxide.

[LAMKIN, RILEY 1991]

$$D_{Si\ in\ Fe\text{-}Si} = 7.35\times10^{-5}(1+12.4\times N_{Si})\exp\left(\frac{-219610\ (J/mol)}{RT}\right)\ m^2/sec$$

[LIM, JEONGYOUN 2006]

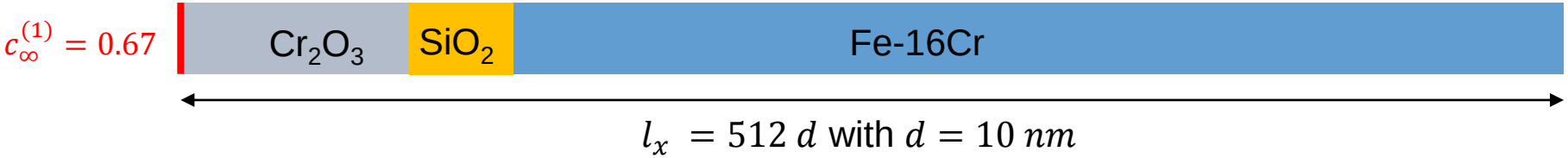
[UEMATSU 2004], [TAKAHASHI 2003], [MATHIOT 2003]

10 orders of magnitude

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Growth kinetics of on oxide layer in 1D

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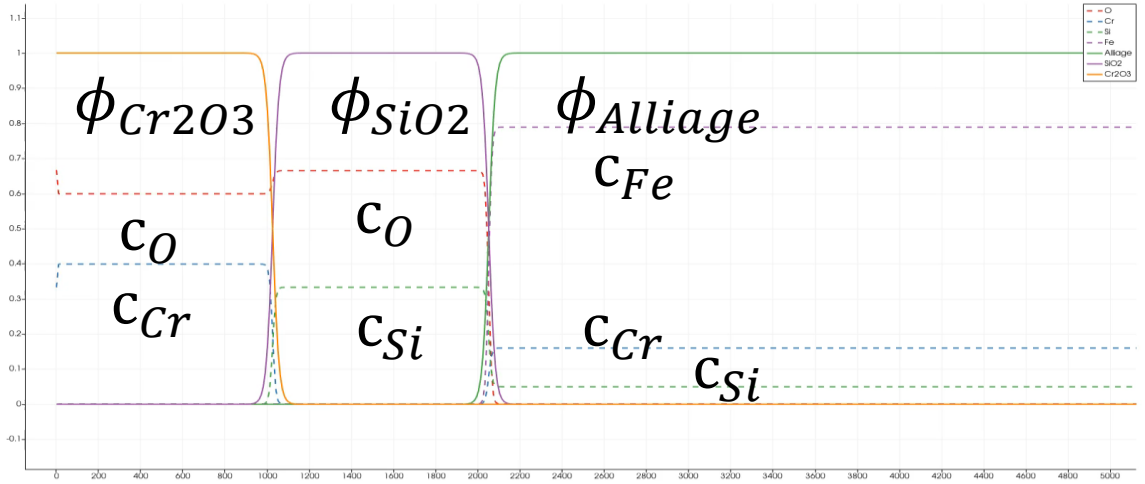
Data are harmonized for the simulations…

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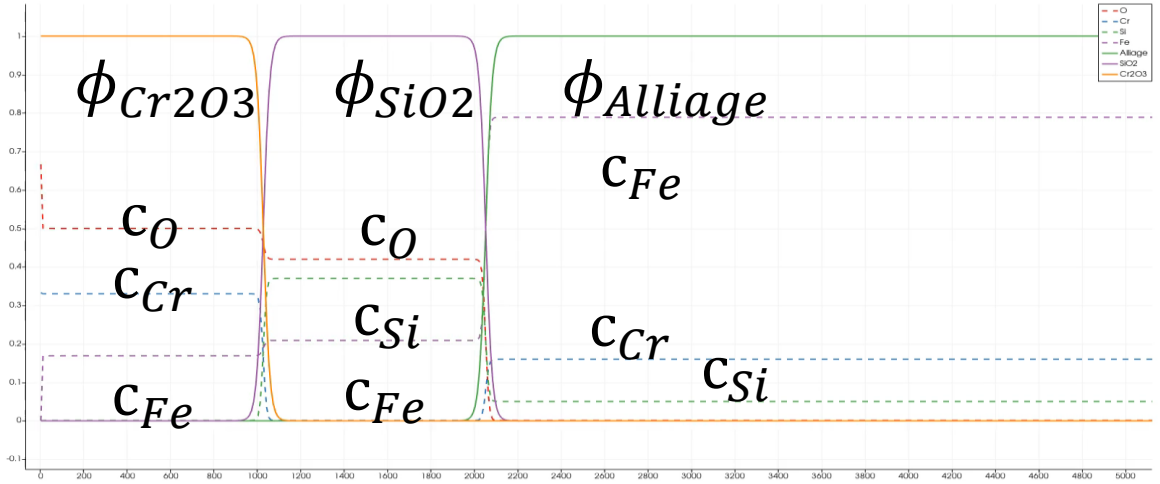
Growth kinetics of on oxide layer in 1D

- **Quaternary case (Cr_2O_3 / SiO_2 / Alloy) without elasticity**

Case $\hat{c}_{Fe}^{(p)} = 0$ in oxide phases



Case $\hat{c}_{Fe}^{(p)} \neq 0$ in oxide phase

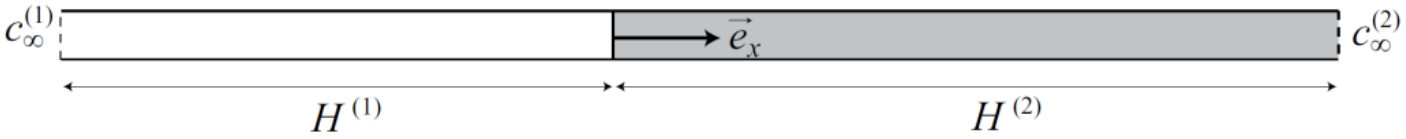


Profiles are very sensitive to the input parameters ; we need reliable data!

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Growth kinetics of on oxide layer in 1D

- **Binary model case (2 phases) *with elasticity***



When "local equilibrium" is assumed, considering $H^{(2)} \gg H^{(1)}$, an asymptotic development of the model can be carried out with elastically isotropic phases (Young modulus $E^{(p)}$, Poisson ratio $\nu^{(p)}$) and a hydrostatic eigenstrain in phase (1) given by $\varepsilon_{ij}^{0(1)} = \varepsilon^* \delta_{ij}$.

When Poisson ratios are equal, one gets:

$$\left(H^{(1)}\right)^2 - H_0^2 = (\kappa_{chem} + \kappa_{elast})\, t \qquad \text{with} \qquad \kappa_{elast} = D^{(1)} \chi^{(1)} \left(\frac{\rho - 3}{1 - \nu}\right) \left(\frac{\varepsilon^*}{\Delta \hat{c}}\right)^2$$

Remark 1: This contribution is quadratic in ε^*

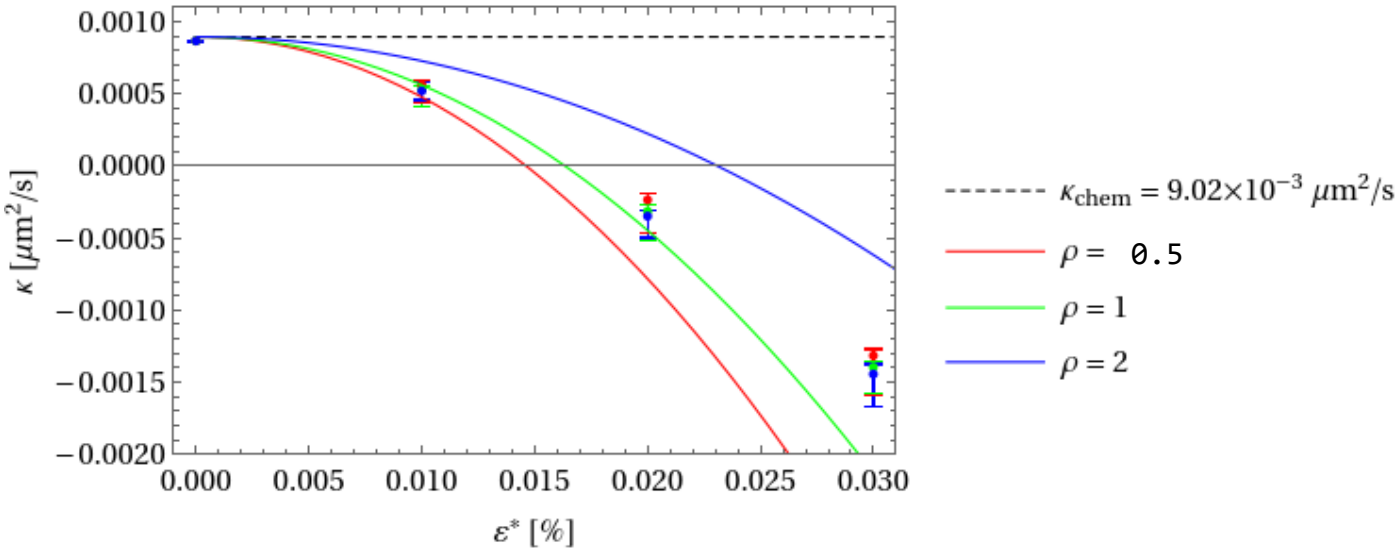
Remark 2: The amplitude is controlled by a "chemo-mechanical" contrast in phase (1): $\chi^{(1)}$

Remark 3 : Change of sign when the mechanical contrast between phases is equal to 3 : ρ

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Growth kinetics of on oxide layer in 1D

- **Binary model case (2 phases) *with elasticity***



1. **The order of magnitude is correct**

2. **The quadratic dependency in ε^* is correctly reproduced → <u>the greater the elastic energy, the less the growth of the oxide layer is favored</u>**

3. Incorrect dependency in ρ… At this stage, we believe there is wrong hypothesis in the analytical derivation about the way diffusion processes are modified by the mechanical fields…

4. Warning: coupling with the mechanical fields inherently perturbates the phase-fields…

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Outline

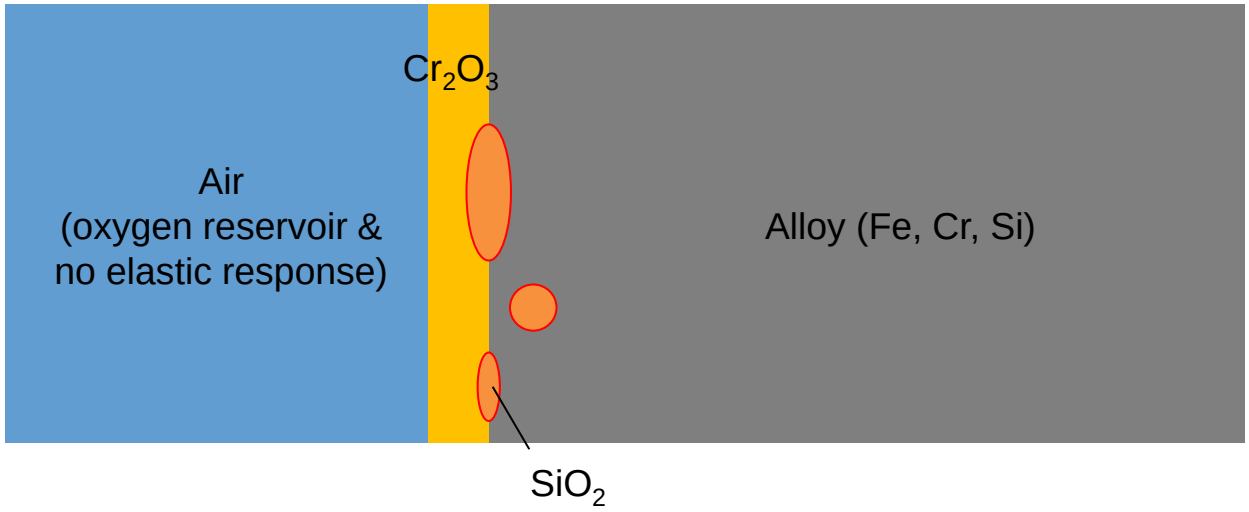
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Conclusion

Conclusion

- **Multi-phase field model → new proposition allowing us to control the properties of interfaces independently and flexibly.**
- **Binary model case (2 phases) without elasticity → Diffusion-controlled kinetics are correctly reproduced.**
- **Ternary and quaternary cases without elasticity → Kinetics and concentration profiles are very sensitive to the input parameters ; we need reliable data!**
- **Binary model case (2 phases) with elasticity → To be continued.**
- Our plane for the coming year:



Thank you!

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